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Electrochemical reduction of derivatives and isomers of ethylpicolinate

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Abstract

Electrolysis of picolinic acid, 2-formylpyridine, 2-hydroxymethylpyridine, ethylnicotinate and ethylisonicotinate in aqueous sulfuric acid solutions was performed on a lead cathode in galvanostatic mode. Electrolyses of picolinic acid, ethylnicotinate and ethylisonicotinate were performed in aqueous solutions to prepare the different hydroxymethylpyridine isomers. Results were compared with those for ethylpicolinate: the chemical yield in 2-hydroxymethylpyridine is lower than that in 3-hydroxymethylpyridine while that in 4-hydroxymethylpyridine is better. Electrolyses of the intermediates 2-formylpyridine and 2-hydroxymethylpyridine in aqueous solutions were performed with a view to understanding the competition between the reduction of the side chain and that of the pyridine nucleus. Study of medium acidity, current density, concentration and temperature shows that electroreduction occurs on the pyridinic nucleus of the formylpyridine and the picoline principally and less on the other derivatives.

1. Introduction

Some alcohols of aromatic heterocyles can be prepared by electrochemical reduction of the corresponding esters or carboxylic acids. Ethylpicolinate, ethylnicotinate and ethylisonicotinate are accessible raw materials, and carboxylic acids can be easily obtained by hydrolysis of the corresponding esters [1–3].

Electrolyses of ethylpicolinate (**1**) in aqueous sulfuric acid solution were performed on a lead cathode in galvanostatic mode [1–4]. The reduction of (**1**) leads to the hemiacetal (**2**), an intermediate not reducible, which gives the reducible 2-formylpyridine (**3**) [1, 5, 6]. The reduction of (**3**) leads to 2-hydroxymethylpyridine (**4**) and picoline (**5**) as follows (Pyr designates the pyridine nucleus):

$$\mathrm{PyrCOOC_2H_5}\,(\mathbf{1}) + 2\,\mathrm{e^-} + 2\,\mathrm{H^+} \rightarrow \mathrm{PyrCHOHOC_2H_5}\,(\mathbf{2}) \quad (1)$$

$$\mathrm{PyrCHOHOC_2H_5}\,(\mathbf{2}) \rightarrow \mathrm{PyrCHO}\,(\mathbf{3}) + \mathrm{C_2H_5OH} \quad (2)$$

$$\mathrm{PyrCHO}\,(\mathbf{3}) + 2\,\mathrm{e^-} + 2\,\mathrm{H^+} \rightarrow \mathrm{PyrCH_2OH}\,(\mathbf{4}) \quad (3)$$

$$\mathrm{PyrCH_2OH}\,(\mathbf{4}) + 2\,\mathrm{e^-} + 2\,\mathrm{H^+} \rightarrow \mathrm{PyrCH_3}\,(\mathbf{5}) + \mathrm{H_2O} \quad (4)$$

The same scheme can be extended to the reductions of the isomers of ethylpicolinate. The corresponding derivatives of ethylnicotinate (**1′**) are noted with index ′ while that of ethylisonicotinate (**1″**) are noted with index ″ (see Table 1).

The electrochemical reduction of picolinic acid (**6**) in sulfuric acid aqueous solutions was studied on lead [2, 6] or cupper amalgam [7] or mercury [8, 9] cathodes. The reduction of (**6**) leads to the hydrate of the 2-formylpyridine (**7**) a non reducible intermediate. The dehydration of (**7**) gives 2-formylpyridine (**3**), which is reduced into 2-hydroxymethylpyridine (**4**) by Reaction (3) [6, 10–18].

$$\mathrm{PyrCOOH}\,(\mathbf{6}) + 2\,\mathrm{e^-} + 2\,\mathrm{H^+} \rightarrow \mathrm{PyrCH(OH)_2}\,(\mathbf{7}) \quad (5)$$

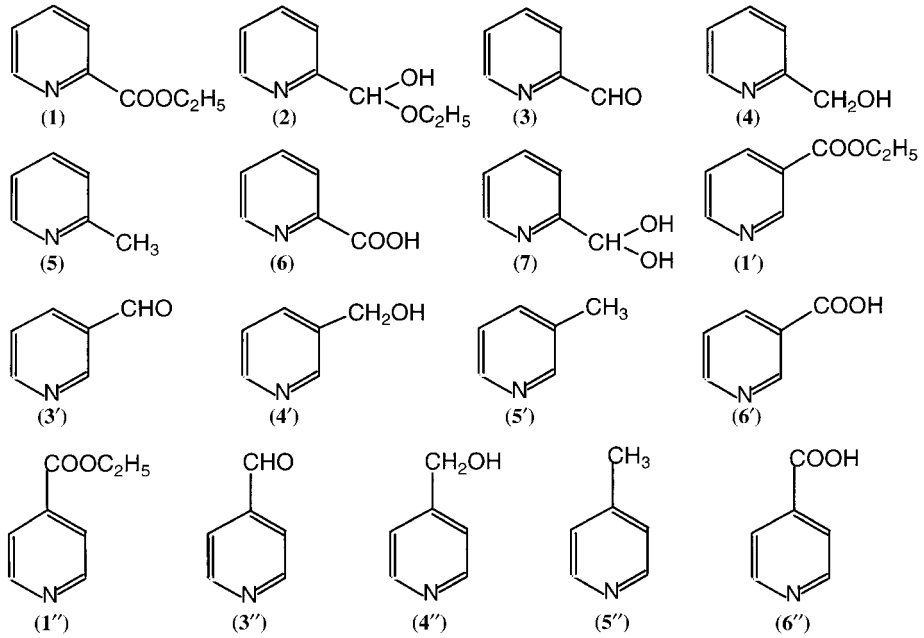
$$\mathrm{PyrCH(OH)_2}\,(\mathbf{7}) \rightarrow \mathrm{PyrCHO}\,(\mathbf{3}) + \mathrm{H_2O} \quad (6)$$

An increase in temperature [1, 6, 19–22] or of the medium acidity [1, 10] accelerates Reactions 2 and 6 and favours the preparation of the alcohols. The reduction of the 2-hydroxymethylpyridine (**4**) into picoline (**5**) by Reaction 4 was studied on a mercury cathode [23].

In parallel to the reduction of the side chain, electrohydrogenation of the nucleus of the different pyridine derivatives may occur [1–4]. This reaction leads to monocyclic or polycyclic derivatives [1, 2, 16, 18, 21, 24–26]. The electrohydrogenation is less important when the acidity of the medium increases [1, 20, 23] and the cathode has a higher hydrogen overpotential [27, 28].

In the present study galvanostatic electrolyses of picolinic acid (**6**), ethylnicotinate (**1′**) and ethylisonicotinate (**1″**), were performed in aqueous sulfuric acid solutions in a divided filter press reactor, with a view to

Table 1. Pyridine derivatives



preparing the corresponding hydroxymethylpyridine isomers, respectively (**4**), (**4′**) and (**4″**). For a better knowledge of the pyridinic nucleus behaviour, the electrolyses of 2-formylpyridine (**3**) and 2-hydroxymethylpyridine (**4**) in aqueous sulfuric acid solutions were also studied under the same conditions.

2. Experimental details

The preparative electrolysis were performed in galvanostatic mode with a microflow cell (Electrocell AB, Sweden) and the electrolytic solutions were assayed by liquid phase chromatography (HPLC). Experimental details are given in [3].

The numbers of moles $n(t)$ of reactants (**6**), (**1′**), (**1″**), (**3**) or (**4**) and products at time t, were determined as functions of the charge $Q(t)$ which is defined by the ratio of the faraday number at t, to n_i° the initial reactant mole number.

Results of the electrolyses are discussed in terms of yield, selectivity, faradaic yield, molar balance, which are functions of time defined below.

The product yield R_j $(j = 3, 3', 3'', 4, 4', 4'', 5, 5', 5'')$ is defined by the ratio $R_j = n_j(t)/n_i^\circ$, where j designates the product and i the reactant.

The selectivity S_4 in relation to the production of the alcohol (**4**) during the electrolyses of picolinic acid (**6**) is defined by the equation: $S_4 = n_4(t)/[n_3(t) + n_4(t) + n_5(t)]$. The selectivities $S_{4'}$ and $S_{4''}$ are defined in the same manner for the production of (**4′**) and (**4″**) from (**1′**) and (**1″**), respectively.

The faradaic yield R_f, is calculated for the electrolyses of picolinic acid (**6**) using the equation: $R_f = [2\,n_3(t) + 4\,n_4(t) + 6\,n_5(t)]F/Q(t)$. The faradaic yields $R_{f'}$ and $R_{f''}$ are also defined for the electrolyses of (**1′**) and (**1″**).

The molar balance B_i for the electrolyses of reactant (**i**) $(i = 6, 1', 1'', 3, 4)$ is defined by the ratio: $B_i = [n_i(t) + \Sigma n_j(t)]/n_i^\circ$. The numerator represents the total mole number of reactant (**i**) and products (**j**) assayed by HPLC. The conversion of reactant (**i**) is expressed by: $\alpha_i = [n_i^\circ - n_i(t)]/n_i^\circ$.

For each electrolysis, the maximum yield in (**j**) is expressed by $R_{j\mathrm{m}}$. In a similar way, the value of the maximum selectivity with respect to the alcohol (**4**) for example is noticed $S_{4\mathrm{m}}$.

The charge values corresponding to the maximum concentration of the aldehyde (**3**) or the alcohol (**4**) are respectively noticed $Q_{3\mathrm{m}}$ and $Q_{4\mathrm{m}}$. The charge value corresponding to the maximum selectivity in relation with the alcohol (**4**) is expressed by $Q'_{4\mathrm{m}}$.

The appearance of an alkane like (**5**) is not immediate after starting an electrolysis, except for the electrolyses of (**4**), and is arbitrarily defined when its concentration is equal or greater to 0.005 mol dm^{-3}. The corresponding charge is indicated by Q_5 and the corresponding values of the molar balance and the faradaic yield are respectively indicated B_5 and R_{f5}. The value of the molar balance corresponding to the maximum yield in (**5**) for the electrolyses of (**4**) is indicated by $B_{5\mathrm{m}}$.

Similar notations are defined with the index prime or second for the corresponding isomers.

3. Results and discussion

3.1. *Electrolyses of carboxylic derivatives*

3.1.1. *Electrolyses of picolinic acid*

For the electrolysis of picolinic acid (**6**) Figure 1 shows the number of moles $n_i(t)$ $(i = 6, 3, 4, 5)$ as a function of the charge $Q(t)$ during an electrolysis performed in a

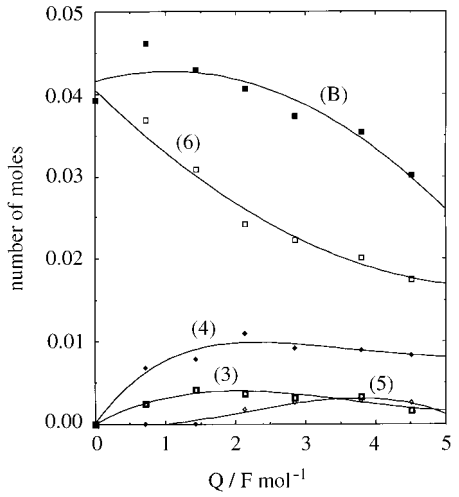


Fig. 1. Variation of the molar numbers as functions of the charge. $C_6^\circ = 0.24\,\text{mol dm}^{-3}$; $j = 1071\,\text{A m}^{-2}$; $\Theta = 50\,^\circ\text{C}$; $C_a = 3\,\text{mol dm}^{-3}$; volume of the catholyte $200\,\text{cm}^3$; cathode area $14\,\text{cm}^2$; (6) picolinic acid (**6**); (3) 2-formylpyridine (**3**); (4) 2-hydroxymethylpyridine (**4**); (5) picoline (**5**); (B) $B \times n_6^\circ$: total molar number assayed by HPLC.

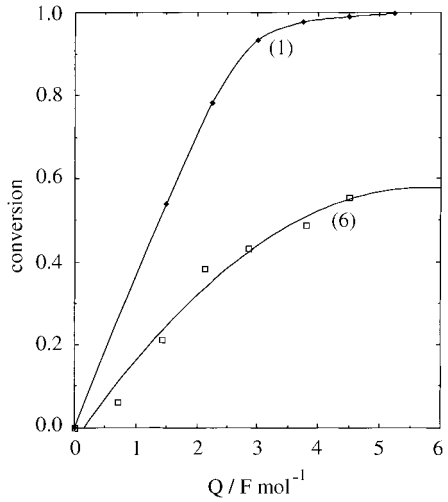


Fig. 2. Variation of the conversion of the 2-ethylpicolinate (**1**) and the picolinic acid (**6**) as functions of the charge. $C_1^\circ = C_6^\circ = 0.24\,\text{mol dm}^{-3}$; $j = 1071\,\text{A m}^{-2}$; $\Theta = 50\,^\circ\text{C}$; $C_a = 3\,\text{mol dm}^{-3}$.

sulfuric acid solution ($C_a = 3\,\text{mol dm}^{-3}$) at $\Theta = 50\,^\circ\text{C}$. The maximum values for $n_3(t)$, $n_4(t)$ and $n_5(t)$ are lower than in the case of (**1**) [1]. (**3**) and (**4**) are formed at the beginning of the electrolysis, (**5**) appears later, before the maximum of (**4**) and next to that of (**3**). When the maximum quantity of (**4**) is reached, the conversion of (**6**), α, is not total. The results are similar for $C_a = 3$ or $5\,\text{mol dm}^{-3}$ and $\Theta = 50$ or $80\,^\circ\text{C}$.

The conversion α increases faster in the case of electrolyses of the ester (**1**) than in the case of the acid (**6**) under the same operating conditions. Figure 2 shows the variation of α for the electrolyses at $\Theta = 50\,^\circ\text{C}$ of (**1**) and (**6**). When Q is $4\,\text{F mol}^{-1}$, α has a value 0.98 for the electrolysis of (**1**) and 0.50 for that of (**6**); note that 10% of (**1**) is hydrolysed into (**6**). An increase in Θ from 50 to $80\,^\circ\text{C}$ causes an increase in α from 0.50 to 0.60 in the case of electrolyses of (**6**); Reaction 6 is accelerated by this temperature increase [6], but α cannot reach a value higher than 0.8 when the electrolyses of (**6**) are conducted at $80\,^\circ\text{C}$. On the other hand, an increase in C_a from 3 to $5\,\text{mol dm}^{-3}$ has no effect on α.

Table 2 gives some results for three electrolyses of picolinic acid (**6**) performed for $C_6^\circ = 0.24\,\text{mol dm}^{-3}$ at $j = 1071\,\text{A m}^{-2}$ at different values of C_a and Θ. The corresponding values for the electrolyses of (**1**) under the same conditions are recalled in order to compare the performances of the preparation of the alcohol (**4**).

In the case of the electrolyses of (**6**), as in that of (**1**) [1], an increase in Θ or C_a produces an increase in the yield R_{4m} and the selectivity S_{4m}, and a decrease in R_{3m}. The Reactions 2 and 6 are accelerated by these effects, thus Reaction 3 is easier. The values of R_{3m} and R_{4m} are lower and those of S_{4m} are higher in the case of the electrolyses of (**6**) than of (**1**). The differences in the results of the electrolyses of (**6**) and (**1**) are probably caused by the difference in the nature of the intermediates (**2**) and (**7**), which are not reducible. (**7**) possibly adsorbs to a lesser extent than (**2**) at the electrode, to explain that (**6**) is less reducible that (**1**) [1, 6].

The values of Q_5 show that (**5**) appears sooner when the acidity or the temperature decreases in the case of the electrolyses of (**6**), but for (**1**) there is no influence of these parameters. Picoline (**5**) appears after the total conversion of (**1**) when for (**6**) it appears for conversion close to 0.50 at $50\,^\circ\text{C}$ and to 0.65 at $80\,^\circ\text{C}$.

When (**5**) appears, the electrohydrogenation of the pyridine nuclei of (**1**), (**6**) and of the reduction products, is not greatly advanced, as shown in Table 2 by the values of B_5 close to 1, except at $80\,^\circ\text{C}$ for (**6**). This table shows that the electrohydrogenation is favoured by an increase in temperature; the products of the electrohydrogenation not being detected by HPLC, the molar balance B_5, is less than 1 in this last case.

R_{f5} has values less than B_5 in the case of (**6**) and close to B_5 in the case of (**1**) (except at $80\,^\circ\text{C}$). The values of R_{f5} are lower for the case of (**6**) than for the case of (**1**).

Table 2. Electrolysis of picolinic acid (**6**) (and ethylpicolinate (**1**) results for different sets of sulfuric acid concentrations and temperatures. $C_6^\circ (= C_1^\circ) = 0.24\,\text{mol dm}^{-3}$; $j = 1071\,\text{A m}^{-2}$, $B_5 = (n_{6\,(\text{or }1)} + n_3 + n_4)/n_{6\,(\text{or }1)}^\circ$. Products: (**3**) aldehyde, (**4**) alcohol, (**5**) alcane

C_a /mol dm^{-3}	Θ /°C	R_{4m}	Q_{4m}	R_{3m}	Q_{3m}	S_{4m}	Q'_{4m}	Q_5	B_5	R_{f5}
3	50	0.27 (0.39)	2.1 (2.3)	0.10 (0.41)	1.5 (2.5)	0.75 (0.49)	1.5 (2.2)	1.6 (2.8)	1.0 (0.87)	0.79 (0.90)
5	50	0.44 (0.57)	2.3 (3.3)	0.05 (0.31)	1.9 (2.5)	0.90 (0.63)	2.2 (3.1)	2.0 (2.8)	1.0 (1.0)	0.63 (1.0)
3	80	0.40 (0.50)	5.2 (3.1)	0.07 (0.13)	2.5 (3.2)	0.92 (0.78)	6.0 (2.6)	5.0 (2.9)	0.75 (0.94)	0.26 (0.78)

An increase in temperature from 50 to 80 °C causes a decrease in R_{f5} in both cases. This result shows that under galvanostatic conditions the proton reduction is favoured in the case of the electrolysis of (**6**) compared to (**1**). It is known that the pyridine derivatives and their nuclei hydrogenation products are catalysts for the proton reduction [7, 12, 29–31]. The catalytic effect is greater in the case of the electrolyses of (**6**) than of (**1**).

3.1.2. *Electrolyses of ethylpicolinate, ethylnicotinate and ethylisonicotinate*

The esters (**1**), (**1′**) and (**1″**) are successively reduced into aldehydes, alcohols and methyl derivatives. The esters are partially hydrolysed into the corresponding carboxylic acids.

The kinetic study of the electrolyses shows that the isomers (**1′**) and (**1″**) react in a similar way to ethylpicolinate. The quantities of aldehydes, alcohols and methylpyridines pass through maximum values. The aldehydes and alcohols appear immediately; the methylpyridines appear rapidly and close to the maximum quantities of the alcohols. The values of yield (in aldehyde, alcohol and carboxylic acid) and of charge corresponding to the maximum quantity of alcohol or aldehyde, the material balance, and the faradaic yield at the appearance of the methylpyridines, are given in Table 3. Figure 3 shows the variation of the yield in alcohol with the charge during the electrolyses of the three isomers.

The hydrolyses of esters (**1**), (**1′**) and (**1″**) give small and practically constant amounts of carboxylic acid during each experiment. Table 3 gives the mean values of the acid yield R_6. This result confirms that the carboxylic acids are less reducible than the corresponding esters. Hydrolysis of isomer (**1′**) is almost impossible.

The chemical yield in alcohol (**4″**) $R_{4''m}$ is greater than that in (**4′**) $R_{4'm}$ which is greater than that in (**4**) R_{4m}. In contrast, (**1**) gives the best yield in aldehyde R_{3m}. The maximum quantity of aldehyde (**3′**) or (**3″**) is obtained before the maximum quantity of alcohol (**4′**) or (**4″**), whereas the maximum quantity of (**3**) is reached after the maximum quantity of (**4**) [1].

Methylpyridine appears before the maximum quantity of alcohol in the case of (**1′**) or (**1″**) in contrast to the case of the ester (**1**). For each ester isomer the material balance and the faradaic yield have close values as the methylpyridine appears: this result shows that the proton reduction only gives the electrohydrogenation of the pyridinic nucleus.

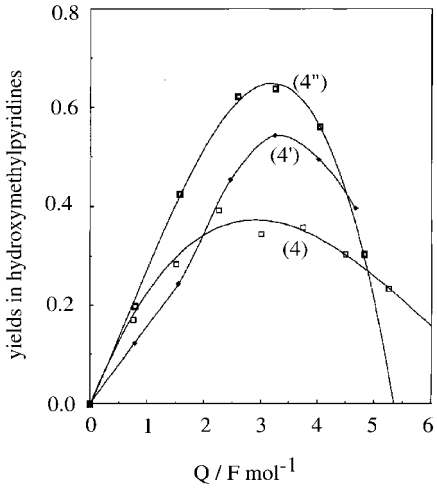


Fig. 3. Variation of the yield of the 2-hydroxymethylpyridine (**4**), the yield of the 3-hydroxymethylpyridine (**4′**) and the yield of the 4-hydroxymethylpyridine (**4″**) as functions of the charge. $C_1^\circ = C_{1'}^\circ = C_{1''}^\circ = 0.24\,\text{mol dm}^{-3}$; $j = 1071\,\text{A m}^{-2}$; $\Theta = 50\,^\circ\text{C}$; $C_a = 3\,\text{mol dm}^{-3}$.

During these experiments, in contrast to the electrolysis of (**1**), no suspension was formed in the solution or viscous layer formed on the cathode. Consequently, derivatives with a hydrogenated nucleus do not form polymers like that obtained in the case of (**1**) [1, 3, 6]. In fact, values of $B_{5''}$ show that hydrogenation of the pyridinic nucleus of (**3″**) has not yet begun when (**5″**) appears. The aldehyde (**3″**) is rapidly reduced to alcohol only, so $R_{4''m}$ is high and $R_{3''m}$ is low. The nucleus electrohydrogenation is easy for both aldehydes isomers (**3**) and (**3′**), especially in the case of (**3′**); see values of R_{3m} and B_5 in Table 3. These results are in accordance with that obtained by Nonaka et al. [23] on a mercury cathode. The difference in the reactivity of the three isomers is due to the steric effect of the side chain of the pyridinic nucleus. If an interaction between the nitrogen atom and the cathode is necessary in order to perform the reduction of the side chain [23], this should be easier in the case of the ester (**1″**) than for (**1**), while the side chain does not prevent the interaction between the nitrogen atom and the lead. In the case of (**1′**) the situation is intermediate. When the reduction of the side chain is difficult, the hydrogenation of the nucleus by proton discharge occurs.

Table 3. Electrolysis of ethylpicolinate (**1**), ethylnicotinate (**1′**) and ethylisonicotinate (**1″**) results. $C_1^\circ = C_{1'}^\circ = C_{1''}^\circ = 0.24$ mol dm^{-3}; $j = 1071$ A m^{-2}; $\Theta = 50$ °C; $C_a = 3$ mol dm^{-3}. $B_5 = (n_{1(1'\text{ or }1'')} + n_{3(3'\text{ or }3'')} + n_{4(4'\text{ or }4'')})/n^\circ_{1(1'\text{ or }1'')}$. Products: (**3**) aldehydes, (**4**) alcohols, (**5**) alcanes, (**6**) acides

Isomer	R_j (j = 6,6′,6″)	R_{jm} (j = 4,4′,4″)	Q_{jm} (j = 4,4′,4″)	R_{jm} (j = 3,3′,3″)	Q_{jm} (j = 3,3′,3″)	Q_j (j = 5,5′,5″)	B_j (j = 5,5′,5″)	R_{fj} (j = 5,5′,5″)
(**1**)	0.10	0.39	2.3	0.41	2.5	2.8	0.87	0.90
(**1′**)	0.03	0.54	3.2	0.04	2.8	2.5	0.69	0.69
(**1″**)	0.12	0.64	3.4	0.15	2.7	2.9	0.97	0.98

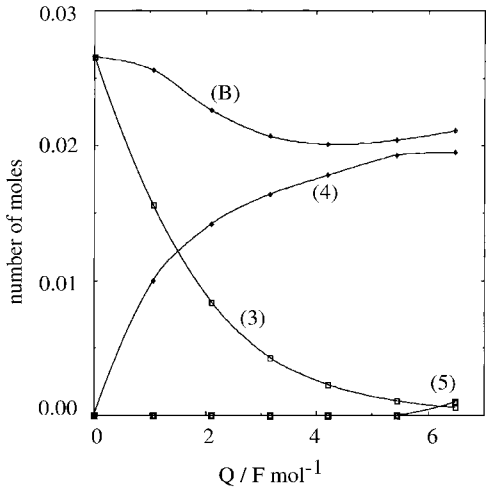


Fig. 4. Variation of the molar numbers as functions of the charge. $C_3^\circ = 0.18\,\text{mol dm}^{-3}$; $j = 1071\,\text{A m}^{-2}$; $\Theta = 80\,^\circ\text{C}$; $C_a = 3\,\text{mol dm}^{-3}$; volume of the catholyte 200 cm^3; cathode area 14 cm^2; (3) 2-formylpyridine (**3**); (4) 2-hydroxymethylpyridine (**4**); (5) picoline (**5**); (B) $B_3 \times n_3^\circ$: total molar number assayed by HPLC.

3.2. *Electrolyses of carbonyl and carbinol derivatives*

The electrolyses of 2-formylpyridine and 2-hydroxymethylpyridine were performed for $C_3^\circ = 0.18\,\text{mol dm}^{-3}$ and $C_4^\circ = 0.14\,\text{mol dm}^{-3}$. C_a takes values between 1 and 5 mol dm^{-3}, j was chosen between 142 and 1071 A m^{-2} and Θ was 50 °C or 80 °C. These values are equivalent to those used for electrolyses of the esters or the picolinic acid for comparison.

Figure 4 shows the variation of the mole numbers $n_i(t)$ $(i = 3, 4, 5)$ and the total mole number of pyridinic derivatives $B_3\, n_3^\circ$ as a function of the charge $Q(t)$ during an electrolysis of the aldehyde (**3**) performed at $j = 1071\,\text{A m}^{-2}$, $C_a = 3\,\text{mol dm}^{-3}$ and $\Theta = 80\,^\circ\text{C}$. The alcohol (**4**) appears immediately after starting the electrolysis and $n_4(t)$ passes through a maximum value; (**5**) appears when the maximum of (**4**) is obtained. It is possible to convert (**3**) completely and to obtain a maximum for $n_5(t)$ by prolonging the electrolysis. The preceding description also applies to electrolyses performed for other values of C_a, j and Θ. The values of R_{4m}, Q_{4m}, B_5 and Q_5 obtained for electrolyses performed with different values of j, C_a and Θ are given in Tables 4 and 5. An increase in C_a or Θ causes an increase in R_{4m} and Q_5; this result is in accordance with an acceleration of Reaction 6. When j increases, R_{4m} and Q_5 decrease and (**5**) appears before the maximum of (**4**); this was previously observed for the electrolyses of (**1**) [1]. When (**5**) appears, B_5 is clearly lower than 1. In aqueous solution the 2-formylpyridine is partially hydrated and the unreactive forms (**2**) and (**7**) are present; thus, the electrohydrogenation of the pyridinic nucleus of (**3**), (**4**) or the hydrate (**7**) and Reaction 3, are favoured compared with Reaction 4. This effect is greater the higher the temperature. The following study sheds further light on this aspect.

Table 4. Electrolysis of 2-formylpyridine. Maximum yield of 2-hydroxymethylpyridine R_{4m} and corresponding charge (Q_{4m}) for different sets of sulfuric acid concentrations, current densities and temperatures. $C_3^\circ = 0.18\,\text{mol dm}^{-3}$

j /A m^{-2}	Θ /°C	C_a/mol dm^{-3}			
		1	2	3	5
142	50			0.62 (1.8)	
285	50	0.04 (1.5)	0.15 (1.5)	0.22 (1.8)	
571	50	0.01		0.015 (4)	0.37 (1.8)
1071	50		0.006 (2.3)	0.01 (4)	0.22 (1.5)
1071	80			0.73 (6)	

Table 5. Electrolysis of 2-formylpyridine. Molar balance at picoline appearance B_5 and corresponding charge (Q_5) for different sets of sulfuric acid concentrations, current densities and temperatures. $C_3^\circ = 0.18\,\text{mol dm}^{-3}$. $B_5 = (n_3 + n_4)/n_3^\circ$

j /A m^{-2}	Θ /°C	C_a/mol dm^{-3}			
		1	2	3	5
142	50			0.77 (1.3)	
285	50	0.81 (1)	0.57 (1)	0.53 (1.2)	
571	50	0.5 (0.5)		0.83 (0.7)	0.81 (1)
1071	50			0.76 (0.1)	0.96 (0.1)
1071	80			0.75 (6)	

During the electrolyses of (**4**) the pyridine (**5**) appears immediately after starting the electrolysis (Figure 4). The mole number $n_5(t)$ passes through a maximum; it is possible to convert (**4**) completely by prolonged electrolysis. The values of R_{5m} and B_{5m} obtained for the electrolyses of (**4**) are given in Table 6. The values of B_{5m} are close to 1: this means that the side chain reduction (4) is favoured compared with the nucleus electrohydrogenation of (**4**). B_4 decreases after the maximum of (**5**), because the electrohydrogenation of (**5**) can occur when the potential of the electrode decreases due to reduction in concentration of (**4**). This result can be explained: the electrohydrogenation of (**5**) is favoured by an increase in j or Θ and does not depend on the acidity of the medium (Table 6).

4. Conclusion

It is possible to prepare hydroxymethylpyridines by electroreduction of the corresponding esters in sulfuric acid medium at a lead cathode. Comparing the isomers,

Table 6. Electrolysis of 2-hydroxymethylpyridine. Maximum yield of picoline R_{5m} and corresponding molar balance B_{5m} for different sets of sulfuric acid concentrations, current densities and temperatures. $C_4^\circ = 0.14\,\text{mol dm}^{-3}$. $B_{5m} = (n_4 + n_5)/n_4^\circ$ for the maximum yield in (**5**)

C_a/mol dm^{-3}	j/A m^{-2}	Θ/°C	R_{5m}	B_{5m}
5	571	50	0.76	1
5	1071	50	0.70	0.95
3	1071	50	0.80	0.95
3	1071	80	0.70	0.93

the 4-hydroxymethylpyridine is obtained with the highest yield and the 2-hydroxymethylpyridine with the lowest.

Picolinic acid is less reducible to alcohol than the corresponding ester. The proton reduction is accelerated in the case of the carboxylic acid compared to the ester. The reduction of 2-hydroxymethylpyridine in picoline occurs sooner in the case of the carboxylic acid compared to the ester at 50 °C, and the electroreduction of the pyridinic nucleus occurs more extensively in the case of the carboxylic acid than of the ester at 80 °C.

During electrolyses of the esters (**1**), (**1′**), (**1″**), the acid (**6**) and the aldehyde (**3**), nucleus electrohydrogenation occurs mainly on the derivatives which are not reducible, like the hemiacetal (**2**) or the hydrate (**7**).

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